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(54) Title: PROCESSES AND CATALYST COMPOSITIONS FOR HYDROCYANATION OF MONOOLEFINS

(57) Abstract

Processes for hydrocyanation of nonconjugated acyclic aliphatic monoolefins, monoolefins conjugated to an ester group, or monoolefins conjugated to a nitrile group which utilize a catalyst precursor composition comprising a bidentate phosphite ligand and zero-valent nickel preferably in the presence of a Lewis acid promoter. Catalyst precursor compositions are also disclosed.

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TITLE

PROCESSES AND CATALYST COMPOSITIONS FOR HYDROCYANATION OF MONOOLEFINS

FIELD OF THE INVENTION

This invention relates to processes and catalyst compositions useful in the hydrocyanation of monoolefins. In particular, the invention relates to the hydrocyanation of monoolefins using zero-valent nickel and a bidentate phosphite ligand in the presence of a Lewis acid promoter.

BACKGROUND OF THE INVENTION

Hydrocyanation catalyst systems, particularly pertaining to the hydrocyanation of olefins, are known in the art. For example, systems useful for the hydrocyanation of butadiene to form pentenenitrile and in the subsequent hydrocyanation of pentenenitrile (PN) to form adiponitrile (ADN), are known in the commercially important nylon synthesis field. The hydrocyanation of olefins using transition metal complexes with monodentate phosphite ligand is documented in the prior art. See for example; U.S. 3,496,215, 3,631,191, 3,655,723 and 3,766,237, and Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; and Stevens, W. R.; Advances in Catalysis, **33**, 1, 1985.

The hydrocyanation of activated olefins such as with conjugated olefins (e.g., butadiene and styrene) and strained olefins (e.g., norbornene) proceeds without the use of a Lewis acid promoter, while hydrocyanation of unactivated olefins such as 1-octene and 3-pentenenitrile requires the use of a Lewis acid promoter. Teachings regarding the use of a promoter in the hydrocyanation reaction appear, for example, in U.S. 3,496,217. This patent discloses an improvement in hydrocyanation using a promoter selected from a large

number of metal cation compounds with a variety of anions as catalyst promoters.

U.S. 3,496,218 discloses a nickel hydrocyanation catalyst promoted with various boron-containing compounds, including triphenylboron and alkali metal borohydrides. U.S. 4,774,353 discloses a process for the preparation of dinitriles, including ADN, from unsaturated nitriles, including PN, in the presence of a zero-valent nickel catalyst and a triorganotin catalyst promoter. U.S. 4,874,884 discloses a process for producing ADN by the zero-valent nickel catalyzed hydrocyanation of pentenenitriles in the presence of a synergistic combination of promoters selected in accordance with the reaction kinetics of the ADN synthesis.

Bidentate phosphite ligands similar to those used in the present invention for the hydrocyanation of monoolefins have been shown to be useful ligands in the hydrocyanation of activated olefins. See, for example: Baker, M. J., and Pringle, P. G.; J. Chem. Soc., Chem. Commun., 1292, 1991; Baker, M. J.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; and Shaw, G.; J. Chem. Soc.; Chem. Commun., 803, 1991, Union Carbide, WO 93,03839.

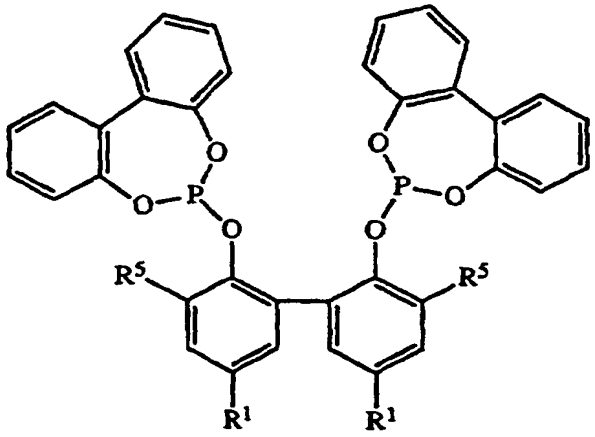
Also, some of the ligands of the present invention have been disclosed with rhodium in catalyst complexes useful for the hydroformylation of functionalized olefins; see, Cuny, G. D., Buchwald, S. L., J. Am. Chem. Soc. 1993, 115, 2066.

The present invention provides for novel processes and catalyst precursor compositions which are more rapid, selective, efficient and stable than current processes and catalyst complexes employed in the hydrocyanation of monoolefins. Other objects and advantages of the present invention will become apparent

to those skilled in the art upon reference to the detailed description of the invention which hereinafter follows.

SUMMARY OF THE INVENTION

The present invention provides a process for hydrocyanation comprising reacting a nonconjugated acyclic aliphatic monoolefin, a monoolefin conjugated to an ester group, e.g., methyl pent-2-eneoate, or a monoolefin conjugated to a nitrile group, e.g., 3-pentenenitrile; with a source of HCN in the presence of a catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand of Formula I,



I

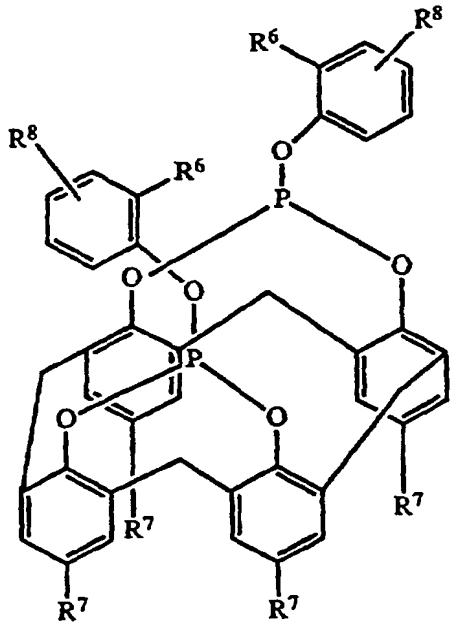
wherein

each R^1 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl;

each R^5 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms;

and wherein said reaction is carried out to produce a terminal organonitrile. Preferably, the reaction is carried out in the presence of a Lewis acid promoter.

The present invention further provides a process for hydrocyanation comprising reacting a nonconjugated acyclic aliphatic monoolefin, a monoolefin conjugated to an ester group, e.g., methyl pent-2-eneoate, or a monoolefin conjugated to a nitrile group, e.g., 3-pentene-nitrile; with a source of HCN in the presence of a catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand of Formulas II, III, IV, or V, as set forth below, and wherein said reaction is carried out to produce a terminal organonitrile. Preferably, the reaction is carried out in the presence of a Lewis acid promoter.

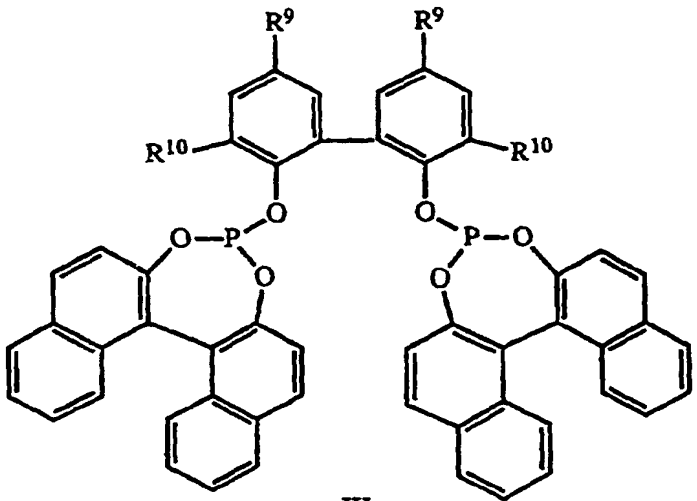


II

wherein

each R^6 and R^7 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms; and

each R^8 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl.

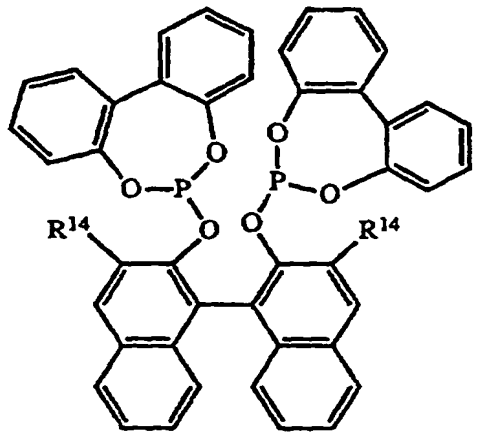


III

wherein

each R^9 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl; and

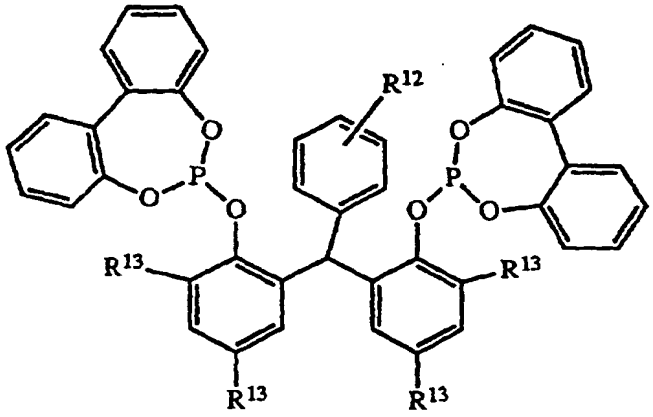
each R^{10} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms.



IV

wherein

each R^{14} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms or $Si(R^{11})_3$ where R^{11} is independently a branched or straight chain alkyl of up to 12 carbon atoms or phenyl.



V

wherein

R^{12} is H or a branched or straight chain alkyl of up to 12 carbon atoms; and

each R^{13} is independently a branched or straight chain alkyl of up to 12 carbon atoms.

The monoolefins of the above-identified processes are described by Formulas VI or VIII, and the corresponding terminal organonitrile compounds produced are described by Formulas VII or IX, respectively.

$$CH_3\text{-}(CH_2)_y\text{-}CH{=}CH\text{-}(CH_2)_x\text{-}R^2 \xrightarrow[\text{promoter, HCN}]{\text{catalyst composition}} NC\text{-}(CH_2)_{y+x+3}\text{-}R^2$$

VI VII

wherein

R^2 is H, CN, CO_2R^3, or perfluoroalkyl;

y is 0 to 12;

x is 0 to 12; and

R^3 is alkyl; or

$$CH_2=CH-(CH_2)_x-R^2 \xrightarrow[\text{promoter, HCN}]{\text{catalyst composition}} NC-(CH_2)_{x+2}-R^2$$

VIII IX

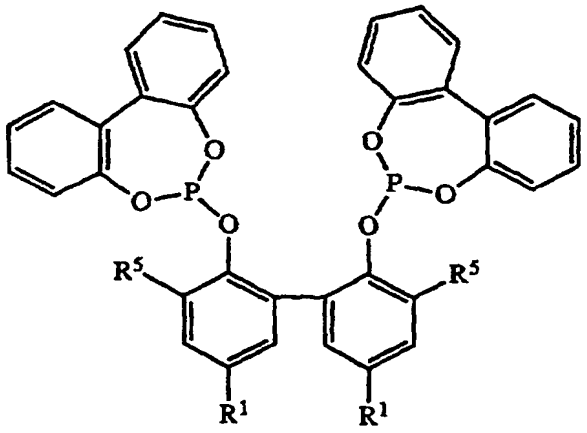
wherein

R^2 is H, CN, CO_2R^3, or perfluoroalkyl;

x is 0 to 12; and

R^3 is alkyl.

The present invention also provides for a catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand of Formula I,



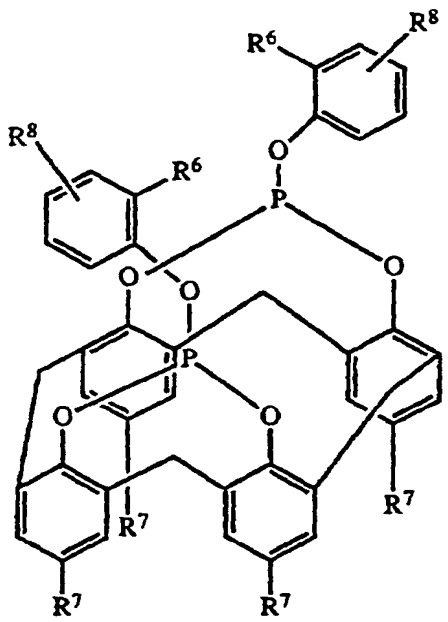
I

wherein

each R^1 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl; and

each R^5 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms.

The present invention further provides for catalyst precursor compositions comprising zero-valent nickel and a bidentate phosphite ligand of Formulas II, III, IV, or V, set forth below.



II

wherein

each R^6 and R^7 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms; and

each R^8 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl.

Hydrocyanation was carried out at 12 cc/min N_2 at 50°C for 5 hours. GC analysis indicated area % of 47.9% ADN and 2.0% of MGN.

EXAMPLE 6

Preparation of (COD)NiL

After removing the solvent from a THF solution of Ligand "A" with $Ni(COD)_2$, ^{31}P NMR in C_6D_6 consisted of two singlets at 178.9 and 146.6 ppm. The resonance at 146.6 ppm corresponded to free Ligand "A". The compound with resonance at 178.9 ppm was determined to be (COD)NiL. A THF solution containing 50 mg (0.18 mmoles) of $Ni(COD)_2$ and 215 mg of ligand (0.27 mmoles) was stirred overnight. A white precipitate formed which was filtered to give 0.206 g of (COD)NiL. ^{31}P NMR in C_6D_6: 178.9 ppm. ^1H NMR in C_6D_6: 7.7 (d, 2H), 7.2 (m, 8H), 7.0 (m, 6H), 6.9 (d, 2H), 6.6 (d, 2H), 4.8 (m, 2H), 4.2 (m, 2H), 2.9 (s, 6H), 2.0 (m) + 1.7 (s) + 1.4 (m) (total area, 26H).

EXAMPLE 7

Preparation of Nickel catalyst from $Ni(acac)_2/AlEt_3$ and ligand

A mixture containing 0.219 g (0.85 mmoles) of $Ni(acac)_2$ (acac = acetylacetonate) and 1.004 g (1.28 mmoles) of Ligand "A" in 12 mL of toluene was cooled to 0°C and 1.3 mL of $AlEt_3$ (25% solution in toluene, 2.5 mmoles) was added. The mixture was warmed to room temperature and then heated to 65°C for 15 minutes. The mixture was stirred overnight, concentrated by vacuum evaporation and hexane added to yield 1.00 g of yellow solid. ^{31}P NMR in C_6D_6: singlets at 169.8 and 162.8 ppm. ^{31}P NMR indicates a 1:1 mixture of NiL_2 and NiL(ethylene).

EXAMPLE 8

Preparation of Nickel catalyst from $Ni(acac)_2/AlEt_3$ and ligand

The procedure of Example 7 was repeated using 2.193 g (8.54 mmoles) of $Ni(acac)_2$, 10.073 g (12.8 mmoles) of Ligand "A" and 12.3 mL (23.4 mmoles) of $AlEt_3$. Hexane addition to the concentrated reaction mixture yielded 5.866 g of gray solid. This material was not soluble in C_6D_6. ^{31}P NMR in THF-d_8 consisted of a singlet at 166.9 ppm. This material was designated sample "8A". The filtrate was concentrated again and hexane added to precipitate out 1.916 g of yellow solid. ^{31}P NMR in C_6D_6: 169.7 ppm. This material was designated sample "8B".

EXAMPLE 9

Preparation of Nickel catalyst from $Ni(acac)_2/AlEt_3$ and ligand

The procedure of Example 8 was repeated using 1.102 g (4.29 mmoles) $Ni(acac)_2$, 5.062 g (6.43 mmoles) of Ligand "A", and 6.5 mL (12.4 mmoles) of $AlEt_3$. The mixture was not heated to 65°C but stirred at room temperature overnight. After concentrating and adding hexane, 4.340 g of yellow solid was isolated. ^{31}P NMR in C_6D_6 matched that of Example 7 but also showed a small peak at 159.4 ppm. NMR indicated a 2:1 ratio of LNi(ethylene): L_2Ni.

EXAMPLE 10

Hydrocyanation of 3-Pentenenitrile using catalyst prepared from Example 7

To 0.175 g (0.12 mmoles of nickel) of sample from Example 7 and 0.190 g (0.24 mmoles) of Ligand "A" were added 5 mL of 3PN and 20 mg (0.04 mmoles) of Ph_3SnOTf. The mixture was treated with HCN at 12 cc/min of N_2 at 50°C. After heating at 50°C for 2.5 hr, the mixture was

heated at 70°C for 0.5 hour. GC analysis using indicated area % of 85.7% ADN and 4.0% of MGN.

EXAMPLE 11

Hydrocyanation of 3-Pentenenitrile using catalyst prepared from Example 8 (8A)

0.175 g (0.11 mmoles of nickel) of sample "8A", and 0.190 g (0.24 mmoles) of Ligand "A" were added to 5 mL of 3-pentenenitrile and 20 mg (0.04 mmoles) of Ph_3SnOTf. The mixture was treated with HCN at 12 cc/min N_2 at 50°C. After 2.5 hour, GC analysis indicated area % of 64.5% of ADN and 2.3% of MGN.

EXAMPLE 12

Hydrocyanation of 3-Pentenenitrile using catalyst prepared from Example 8 (8B)

175 mg (0.11 mmoles of nickel) of sample "8B" and 190 mg (0.24 mmoles) of Ligand "A" in 5 mL of 3PN was added to 20 mg (0.04 mmoles) of Ph_3SnOTf. The mixture was treated with HCN at 12 cc/min N_2 at 50°C. After 3 hours, GC analysis indicated area % of 21.9% ADN and 2.5% MGN.

EXAMPLE 13

Hydrocyanation of 3-Pentenenitrile using catalyst prepared from Example 9

To 0.175 g (0.15 mmoles of nickel) of the product from Example 9 and 0.190 g (0.24 mmoles) of Ligand "A" were added 5 mL of 3-pentenenitrile and 20 mg (0.04 mmoles) of Ph_3SnOTf. 500 mg of HCN in 2 mL of toluene was added and the mixture heated to 50°C. After 1 hour, GC analysis indicated mole % of 37.4% ADN and 2.2% MGN. Another 500 mg of HCN in 2 mL of toluene was added and the mixture stirred at 70°C overnight. GC analysis indicated mole % of 64.7% ADN and 3.7% MGN.

EXAMPLE 14

Hydrocyanation of 3-Pentenenitrile without promoter

170 mg (0.22 mmoles) of Ligand "A" and 20 mg (0.073 mmoles) of $Ni(COD)_2$ were dissolved in 5 mL of THF. The solvent was removed by vacuum evaporation. To the mixture was added 5 mL of 3-pentenenitrile. The mixture was hydrocyanated at 12 cc/min N_2 at 50°C. After two hours, GC analysis indicated area % of 1.5% ADN, 0.1% MGN and 0.02% of 2-ethylsuccinonitrile (ESN).

EXAMPLE 15

Hydrocyanation of

Methyl-3-Pentenoate with Ph_3SnOTf promoter

170 mg (0.10 mmoles) of LNi (ethylene) and NiL_2 in a mole ratio of 1:1.5 and 190 mg (0.24 mmoles) of Ligand "A" were added 5 mL of methyl-3-pentenoate. To this mixture was added 20 mg (0.04 mmoles) of Ph_3SnOTf. The mixture was hydrocyanated at 12 cc/min N_2 at 50°C for 2 hours and at 70°C for 2 hours. After this time, GC analysis indicated area % of 0.8% 3-cyanomethyl-valerate; 3.5% of 4-cyano-methylvalerate and 59.9% of 5-cyanomethylvalerate.

EXAMPLE 16

Hydrocyanation of

1-octene with zinc chloride promoter

To 5 mL of THF was added 340 mg (0.43 mmoles) of Ligand "A" and 40 mg (0.14 mmoles) of $Ni(COD)_2$. The solvent was removed and 3 mL of toluene, 2 mL of 1-octene and 10 mg (0.073 mmoles) of $ZnCl_2$ were added. The mixture was hydrocyanated at 12 cc/min N_2 at 60°C. After 2 hours, GC analysis indicated area % of 16% n-octylcyanide.

EXAMPLE 17

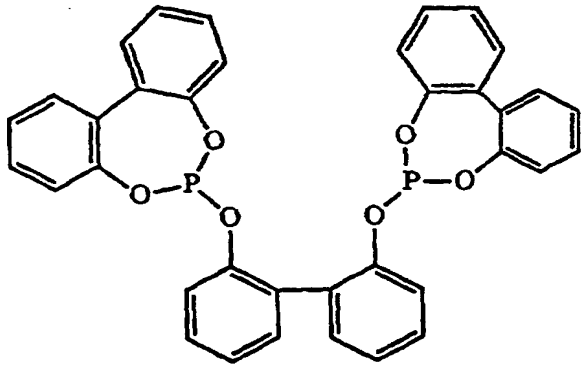
Hydrocyanation of perfluorobutyulethylene

To 5 mL of THF was added 340 mg (0.43 mmoles) of Ligand "A" and 40 mg (0.14 mmoles) of $Ni(COD)_2$. The

solvent was removed and 5 mL of toluene, 2 mL of perfluorobutylethylene and 10 mg (0.073 mmoles) of $ZnCl_2$ were added. The mixture was hydrocyanated at 12 cc/min N_2 at 40°C. After 0.5 hours, GC analysis indicated that all of the olefin has been converted to perfluorobutyl-CH_2CH_2-CN.

COMPARATIVE EXAMPLE 18

Hydrocyanation using bidentate Ligand "B"

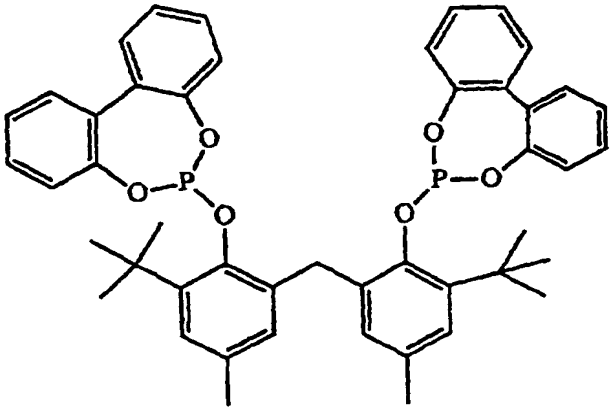


Ligand "B"

75 mg (0.12 mmoles) of the above Ligand "B" and 20 mg (0.07 mmoles) of $Ni(COD)_2$ were dissolved in 5 mL of THF and the solvent was removed. 5 mL of 3-pentenenitrile and 10 mg (0.073 mmoles) of $ZnCl_2$ were added. The mixture was treated with HCN at 40°C at 30 cc/min N_2. No conversion to adiponitrile was observed after 1.5 hours. The procedure was repeated but with 0.150 g (0.24 mmoles) of the above Ligand "B" and HCN at 30 cc/min N_2 at 50°C for 15 min., 60°C for 15 min and 70°C for 15 min. After this time, no adiponitrile was observed.

COMPARATIVE EXAMPLE 19

Hydrocyanation using Ligand "C"



Ligand "C"

To 160 mg (0.21 mmoles) of the above Ligand "C" and 20 mg (0.07 mmoles) of $Ni(COD)_2$ was added 5 mL THF. The solvent was removed and 5 mL of 3-pentenenitrile and 10 mg (0.073 mmoles) of $ZnCl_2$ were added. Hydrocyanation was done at 30 cc/min N_2 at 50°C for 15 min, 60°C for 15 min and 70°C for 15 min. No adiponitrile product was generated.

EXAMPLE 20

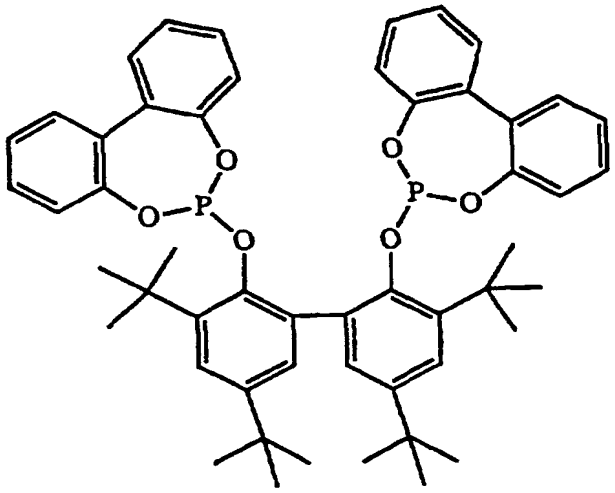
Hydrocyanation of 2-Pentenenitrile

A mixture of NiL_2 (L = Ligand "A") (0.100 g; 0.06 mmol), $Ph_3Sn(O_3SCF_3)$ (0.030 g; 0.06 mmol), cis-2-pentenenitrile (.017 g; 0.21 mmol) in benzene (1.30 mL) and acetonitrile (0.50 mL) was heated (71°C) with stirring under nitrogen atmosphere in a septum capped glass vial. HCN (50 uL of 2.55M HCN in benzene; 0.0034 g HCN; 0.13 mmol) was injected into the mixture and aliquots removed periodically and analyzed by GC. After 1 hr, the mixture contained 2-pentenenitrile (0.082 mmol), adiponitrile (0.110 mmol), 2-methyl-

glutaronitrile (0.006 mmol), 2-ethylsuccinonitrile (0.002 mmol), and valeronitrile (0.007 mmol).

EXAMPLE 21

Hydrocyanation using Ligand "D"

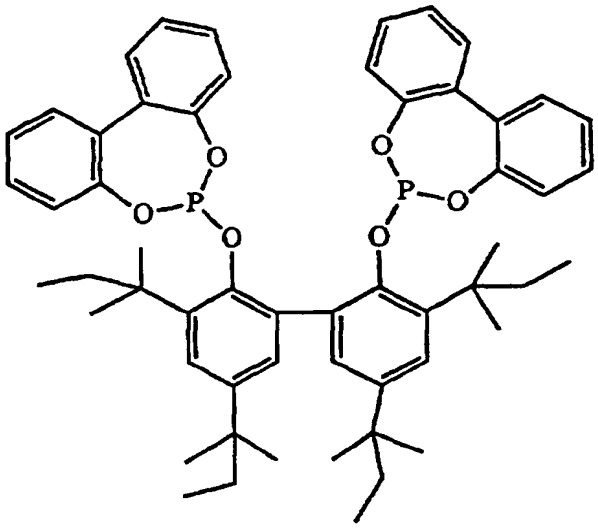


Ligand "D"

This ligand, D, was prepared similarly to Ligand "A" starting with the oxidation of 2,4-di-t-butylphenol to give the biphenol followed by the reaction with 1,1'biphenyl-2,2'-diyl phosphoro-choloridite. n-BuLi was used as the base instead of NEt_3. 369 mg of Ligand "D" and 40 mg of $Ni(COD)_2$ were dissolved in 5 mL of THF and the solvent removed. 5 mL of 3PN and 20 mg of $ZnCl_2$ were added. The mixture was treated with HCN at 80°C at 12 cc/min N_2. After 1.5 hr, 31.1% of ADN, 7.9% of MGN and 0.8% of ESN were obtained as determined by GC analysis.

EXAMPLE 22

Hydrocyanation using Ligand "E"



Ligand "E"

This ligand, E, was prepared similarly to Ligand "A" starting with the air oxidation of 2,4-di-t-pentylphenol to give the biphenol followed by treatment with 1,1'biphenyl-2,2'-diyl phosphorochloridite. n-BuLi was used as the base instead of NEt_3. ^{31}P NMR in C_6D_6: 145.1 ppm. 380 mg of Ligand "E" and 40 mg of $Ni(COD)_2$ were dissolved in 5 mL of THF and the solvent removed. 5 mL of 3PN and 20 mg of $ZnCl_2$ were added. The mixture was treated with HCN at 50, 60, 70, 80, and 100°C for 15 minutes each at 12 cc/min N_2. After heating at 100°C, 36.8% of ADN, 8.5% of MGN and 0.9% of ESN were obtained as determined by GC analysis.

EXAMPLES 23 to 57

Use of other Lewis Acid Promoters in the Hydrocyanation of 3-Pentenenitrile [L = Ligand "A"]

A mixture NiL_2 (0.230 g; 0.14 mmol) and L (0.110 g; 0.14 mmol), 3-pentenenitrile (5.0 mL; 52 mmol), and a Lewis acid promoter (0.14 mmol) (indicated in the Table)

was heated at 70°C and treated with HCN via vapor transfer as described above (N_2 flow = 12 cc/min) for 2 hours. The results in terms of percent conversion and percent selectivity are presented in the Table below. Conversion and selectivity are defined as follows:

Conversion = 100 x (ADN + MGN + ENS)/(initial 3PN)

Selectivity = 100 x ADN/(ADN + MGN + ESN)

where ADN is adiponitrile, MGN is 2-methylglutaronitrile, ESN is 2-ethylsuccinonitrile, and 3PN is 3-pentenenitrile.

TABLE

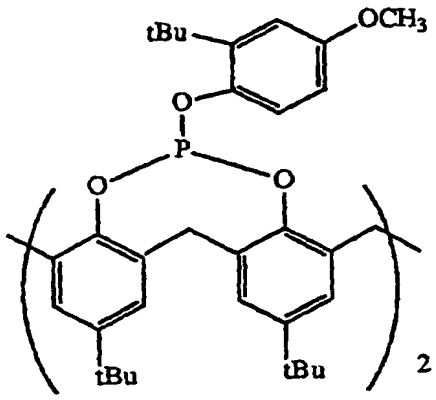
Ex.	Promoter	Conversion %	Selectivity %
23	$ZnBr_2$	26	83
24	ZnI_2	59	82
25	$ZnCl_2$	64	76
26	$ZnSO_4$	31	79
27	$CuCl_2$	7	89
28	CuCl	13	80
29	$Cu(O_3SCF_3)_2$	4	95
30	$CoCl_2$	28	74
31	CoI_2	28	79
32	FeI_2	25	79
33	$FeCl_3$	14	71
34	$FeCl_2(THF)_2$*	52	75
35	$TiCl_4(THF)_2$*	12	87
36	$TiCl_4$	25	80
37	$TiCl_3$	24	85
38	$MnCl_2$	41	79
39	$ScCl_3$	13	88
40	$AlCl_3$	15	85
41	$(C_8H_{17})AlCl_2$	26	82
42	$(i\text{-}C_4H_9)_2AlCl$	3	83
43	Ph_2AlCl	13	81
44	$ReCl_5$	22	97

45	$ZrCl_4$	25	87
46	$NbCl_5$	2	85
47	VCl_3	7	85
48	$CrCl_2$	1	80
49	$MoCl_5$	3	78
50	YCl_3	48	88
51	$CdCl_2$	60	80
52	$LaCl_3$	31	87
53	$Er(O_3SCF_3)_3$	34	90
54	$Yb(O_2CCF_3)_3$	36	84
55	$SmCl_3$	40	83
56	BPh_3	40	95
57	$TaCl_5$	4	85

*Tetrahydrofuran

EXAMPLE 58

Preparation of the Ligand of Formula II where R^6 and R^7 are t-butyl and R^8 is OCH_3 (Ligand "F")



Ligand "F"

To 1.44 g of the dichlorodite derived from PCl_3 and 2-t-butyl-4-methoxyphenol in 20 mL of toluene was added 1.66 g of 4-t-butylcalix[4]arene and 1.3 g of triethyl amine in 20 mL of toluene. The mixture was stirred overnight and refluxed for one hour. The cooled mixture

was filtered through celite, washed with toluene and solvent removed to give 2.04 g of the desired product as a white solid. ^{31}P {1H} (121.4 MHz, C_6D_6): 116.06 ppm.

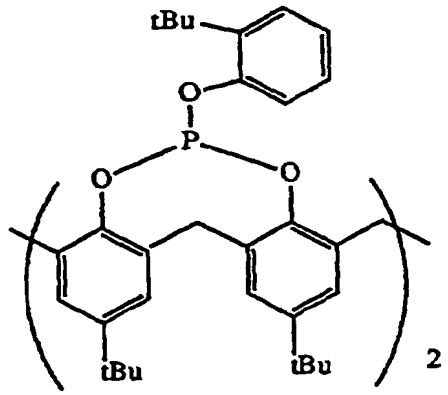
EXAMPLE 59

Hydrocyanation Using Ligand "F"

464 mg of Ligand "F" and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of tetrahydrofuran. The solvent was removed and 20 mg of $ZnCl_2$ and 5 mL of 3-pentenenitrile (3-PN) were added. The mixture was treated with HCN with a nitrogen flow rate of 12 cc/min. The oil bath was initially at 50°C. After 15 minutes, the temperature controller was set at 60°C. After 15 minute intervals, the temperature controller was set at 70, 80, and 100°C. After 15 minutes at the last temperature setting, GC analysis indicated 19.0% adiponitrile (ADN), 6.3% 2-methylglutaronitrile (MGN) and 3.8% 2-ethyl-succinonitrile (ESN).

EXAMPLE 60

Preparation of the Ligand of Formula II where R^6 and R^7 are t-butyl and R^8 is H (Ligand "G")



Ligand "G"

To 1.22 g of dichlorodite derived from PCl_3 and 2-t-butylphenol in 20 mL of toluene was added 1.66 g of 4-t-butylcalix[4]arene and 1.3 g of triethylamine in

20 mL of toluene. The mixture was stirred overnight and refluxed for one hour. The cooled mixture was filtered through celite, washed with toluene and solvent removed to give 1.926 g of the desired product as a white solid. ^{31}P {1H} (121.4 MHz, C_6D_6): 115.6 ppm.

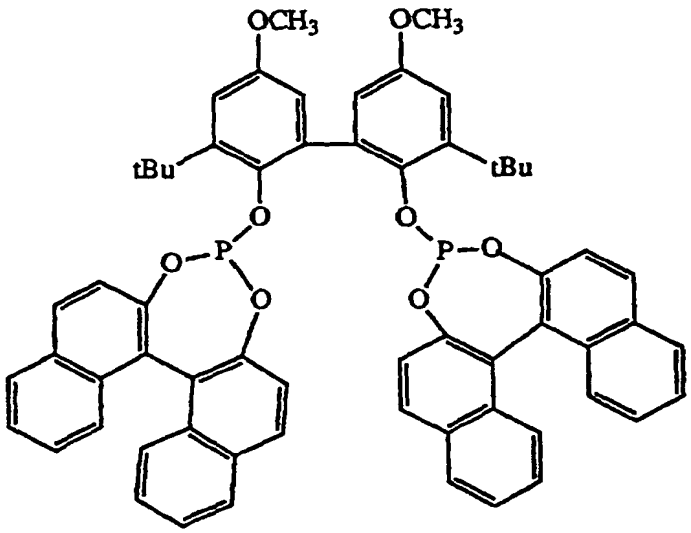
EXAMPLE 61

Hydrocyanation Using Ligand "G"

342 mg of Ligand "G" and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of tetrahydrofuran. The solvent was removed and 20 mg of $ZnCl_2$ and 5 mL of 3PN were added. The mixture was treated with HCN with a nitrogen flow rate of 12 cc/min. The oil bath was initially at 50°C. After 15 minutes, the temperature controller was set at 60°C. After 15 minute intervals, the temperature controller was set at 70, 80, and 100°C. After 15 minutes at the last temperature setting, GC analysis indicated 17.1% ADN, 6.4% MGN, and 5.9% ESN.

EXAMPLE 62

Preparation of the Ligand of Formula III where R^9 is OCH_3 and R^{10} are t-butyl (Ligand "H")



Ligand "H"

To 0.7 mL of PCl_3 in 15 mL of toluene at 0°C was added 2.3 g of 1,1'-bi-2-naphthol and 4.1 mL of triethylamine in 20 mL of toluene. The mixture was stirred at room temperature. To 1.43 g of 2,2'-dihydroxy-3,3'-di-t-butyl-5,,5'-dimethoxy-1,1'-biphenyl in 15 mL of toluene at -20°C was added 4.5 mL of 1.77 M n-butyl lithium in hexane. The mixture was stirred at room temperature for one hour and the above chlorodite solution was added. The mixture was stirred overnight and then filtered through celite, washed with toluene and solvent removed to give 4.044 g of the product as a light yellow solid. ^{31}P {1H} (121.4 MHz, C_6D_6): 146.84, 146.74, 146.62, 146.20, 146.10, 145.76, 145.41, 145.00, and 144.89 ppm. FABMS: Found: M+H 987.10; Calculated for $C_{62}H_{52}O_8P_2$ + H: 987.32.

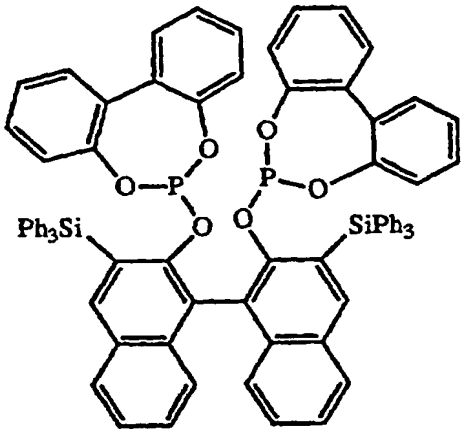
EXAMPLE 63

Hydrocyanation Using Ligand "H"

445 mg of Ligand "H" and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of tetrahydrofuran. The solvent was removed and 20 mg of $ZnCl_2$ and 5 mL of 3PN were added. The mixture was treated with HCN with a nitrogen flow rate of 12 cc/min. The temperature bath was initially at 50°C. After 15 minutes, the temperature controller was set at 60°C. After 15 minute intervals, the temperature controller was set at 70, 80, and 100°C. After 15 minutes at the last temperature setting, GC analysis indicated 37.1% ADN, 5.0% MGN, and 0.9% ESN.

EXAMPLE 64

Preparation of the Ligand of Formula IV where R^{14} is triphenyl silyl (Ligand "J")



Ligand "J"

Chloridite (0.34 g/1.37 mmol) derived from 2,2'-biphenol and PCl_3 was dissolved in toluene (10 mL) and the solution was cooled to -40°C. 3,3'-Triphenylsilyl-1,1'-bi-2-naphthol (0.80 g/0.68 mmol) and triethylamine (0.5 mL) were dissolved in toluene (15 mL) and this solution was added dropwise to the cold

solution. The mixture was stirred overnight at room temperature. The solids were filtered and the solvent was removed to give 0.65 g of a light yellow solid. ^{31}P NMR ($CDCl_3$): δ 146.23 (small peak), 136.37 (major peak) and 13 (small peak).

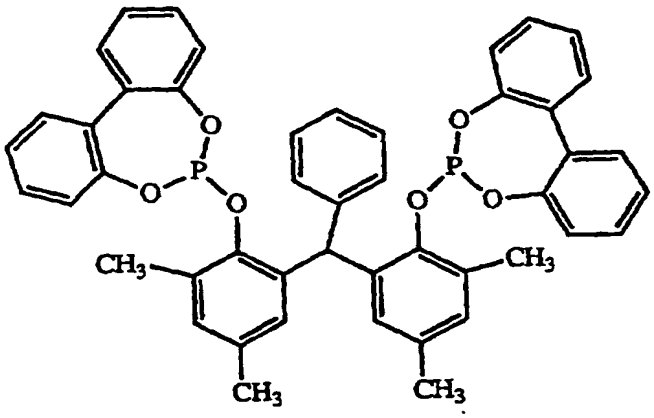
EXAMPLE 65

Hydrocyanation Using Ligand "J"

517 mg of Ligand "J", 0.020 g of $ZnCl_2$ and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of 3PN. The mixture was treated with HCN with a nitrogen flow rate of 30 cc/min at 70°C for one hour. GC analysis indicated 9.3% ADN, 0.6% MGN, and 0.1% ESN.

EXAMPLE 66

Preparation of the Ligand of Formula V where R^{12} is H and each R^{13} is CH_3 (Ligand "K")



Ligand "K"

To 2.0 g of the chloridite derived from 2,2'-biphenol and PCl_3 in 20 mL of toluene was added 1.95 g of 2,2'-benzylidenebis(4,6-dimethylphenol) (prepared by the procedure of Yamada, F.; Nishiyama, T.; Yamamoto, M.; and Tanaka, K.; Bull. Chem. Soc. Jpn., 62, 3603 (1989)) and 2 g of triethylamine in 20 mL of toluene. The mixture was stirred overnight and refluxed

for one hour. The cooled mixture was filtered through celite, washed with toluene and solvent removed to give 3.912 g of the desired product as a tan solid. ^{31}P {1H} (121.4 MHz, C_6D_6): 148.00 ppm.

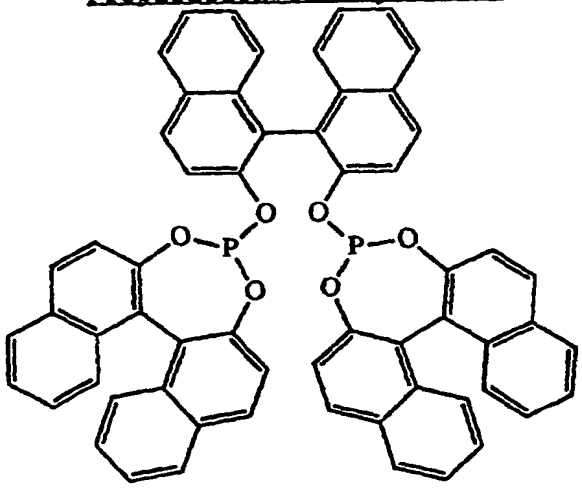
EXAMPLE 67

Hydrocyanation Using Ligand "K"

327 mg of Ligand "K" and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of tetrahydrofuran. The solvent was removed and 20 mg of $ZnCl_2$ and 5 mL of 3PN were added. The mixture was treated with HCN with a nitrogen flow rate of 30 cc/min at 70°C for one hour. GC analysis indicated 12.9% ADN, 42.% MGN, and 0.4% ESN.

COMPARATIVE EXAMPLE 68

Preparation of Ligand "L"



Ligand "L"

Ligand "L" was prepared according to the procedure described in Example 6 of WO 93/03839, with the exception that the weight of PCl_3 listed in the literature procedure did not correspond to the number of moles of PCl_3 needed, so the appropriate adjustment was made. Phosphorus trichloride (0.32 g; 2.3 mmol) was dissolved in toluene (10 mL) and the solution was cooled to 0°C. S-1-1'-bi-2-naphthol (1.0 g; 3.5 mmol) and

to 0°C. S-1-1'-bi-2-naphthol (1.0 g; 3.5 mmol) and triethylamine (0.8 mL; 6.0 mmol) were dissolved in toluene (30 mL) and this solution was added dropwise to the PCl_3 solution. The mixture was then heated to reflux for 2 hours. The solids were filtered off and the solvent was removed to give 0.8 g of white solid. ^{31}P NMR ($CDCl_3$): δ 145.4.

COMPARATIVE EXAMPLE 69

Hydrocyanation Using Ligand "L"

384 mg of Ligand "L", 0.020 g of $ZnCl_2$ and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of 3PN. The mixture was treated with HCN with a nitrogen flow rate of 30 cc/min at 70°C for one hour. GC analysis indicated 1.8% ADN, 0.8% MGN, and 0.2% ESN.

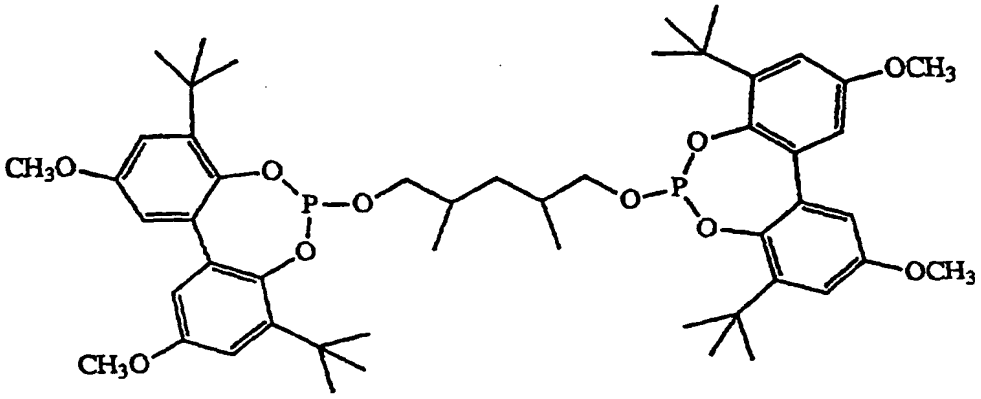
COMPARATIVE EXAMPLE 70

Hydrocyanation Using Ligand "L"

384 mg of Ligand "L", 0.020 g of $ZnCl_2$ and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of 3PN. The mixture was treated with HCN with a nitrogen flow rate of 30 cc/min at 70°C for one hour. GC analysis indicated 3% ADN, 1.5% MGN, and 0.3% ESN.

COMPARATIVE EXAMPLE 71

Preparation of Ligand "M"



Ligand "M"

Ligand "M" was prepared according to the procedure described in Example 1 of WO 93/03839. Phosphorus trichloride (0.66 g; 4.8 mmol) was dissolved in toluene (15 mL) and cooled to 0°C. The 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl (1.72 g; 4.8 mmol) and triethylamine (2.7 mL; 19.2 mmol) were dissolved in toluene (25 mL). This solution was added dropwise to the cold PCl_3 solution. After the addition was complete, the mixture was heated to reflux for 1.5 hrs. The mixture was then cooled to 0°C, and solid (2R,4R)-(-)-pentanediol (0.25 g; 2.4 mmol) was added. The mixture was again heated to reflux for 1.5 hrs., and then stirred overnight at room temperature. The solids were filtered, and the toluene was removed in vacuo. The resulting yellow solid was dissolved in hot CH_3CN (approx. 10 mL) and stirred at room temperature. The resulting white solid was removed, washed with cold CH_3CN, and dried. 1.3 g of material was collected. ^{31}P NMR ($CDCl_3$): δ 146.2.

COMPARATIVE EXAMPLE 72

Hydrocyanation Using Ligand "M"

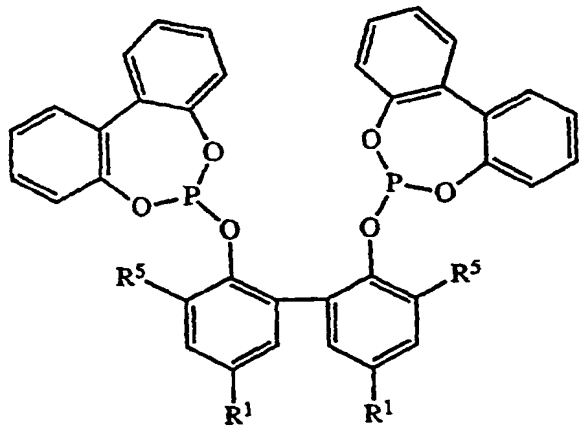
368 mg of Ligand "M", 0.020 g of $ZnCl_2$ and 0.040 g of $Ni(COD)_2$ were dissolved in 5 mL of 3PN. The mixture was treated with HCN with a nitrogen flow rate of 30 cc/min at 70°C for one hour. GC analysis indicated 0.0% ADN, 0.2% MGN, and 0.0% ESN.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than the foregoing specification, as indicating the scope of the invention.

CLAIMS

We Claim:

1. A process for hydrocyanation, comprising reacting a nonconjugated acyclic aliphatic monoolefin, monoolefin conjugated to an ester group or monoolefin conjugated to a nitrile group with a source of HCN in the presence of a catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand of Formula I,



I

wherein

each R^1 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl;

each R^5 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms;

and wherein said reaction is carried out to produce a terminal organonitrile.

2. The process of Claim 1 wherein the reaction is carried out in the presence of a Lewis acid promoter.

3. The process of Claims 1 or 2 wherein the nonconjugated acyclic aliphatic monoolefin, monoolefin

conjugated to an ester group or monoolefin conjugated to a nitrile group are compounds of Formula VI

$$CH_3\text{-}(CH_2)_y\text{-}CH{=}CH\text{-}(CH_2)_xR^2$$

VI

wherein

R^2 is H, CN, CO_2R^3, or perfluoroalkyl;

y is 0 to 12;

x is 0 to 12; and

R^3 is alkyl;

and the terminal organonitrile product is a compound of Formula VII

$$NC\text{-}(CH_2)_{y+x+3}\text{-}R^2$$

VII

wherein

R^2, y and x are as defined above.

4. The process of Claims 1 or 2 wherein the nonconjugated acyclic aliphatic monoolefin, monoolefin conjugated to an ester group or monoolefin conjugated to a nitrile group are compounds of Formula VIII

$$CH_2{=}CH\text{-}(CH_2)_x\text{-}R^2$$

VIII

wherein

R^2 is H, CN, CO_2R^3, or perfluoroalkyl;

x is 0 to 12; and

R^3 is alkyl,

and the terminal organonitrile product is a compound of Formula IX

$$NC\text{-}(CH_2)_{x+2}\text{-}R^2$$

IX

wherein

R^2 and x are as defined above.

5. The process of Claims 1 or 2 wherein each R^1 is OR^4 wherein R^4 is independently methyl, ethyl, isopropyl, or t-butyl.

6. The process of Claim 5 wherein each R^1 is OR^4 wherein R^4 is methyl.

7. The process of Claims 1 or 2 wherein the nonconjugated acyclic aliphatic monoolefin, monoolefin conjugated to an ester group or monoolefin conjugated to a nitrile group is 2-pentenenitrile, 3-pentenenitrile, 4-pentenenitrile, alkyl 2-penteneoate, alkyl 3-penteneoate, alkyl 4-penteneoate, or a compound $C_xF_{2x+1}CH=CH_2$ wherein x is 1 to 12.

8. The process of Claims 1 or 2 wherein the terminal organonitrile is adiponitrile, alkyl 5-cyanovalerate, 3-(perfluoroalkyl)propionitrile, or a compound $C_xF_{2x+1}CH_2CH_2CN$ wherein x is 1 to 12.

9. The process of Claim 2 wherein the Lewis acid promoter is an inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin.

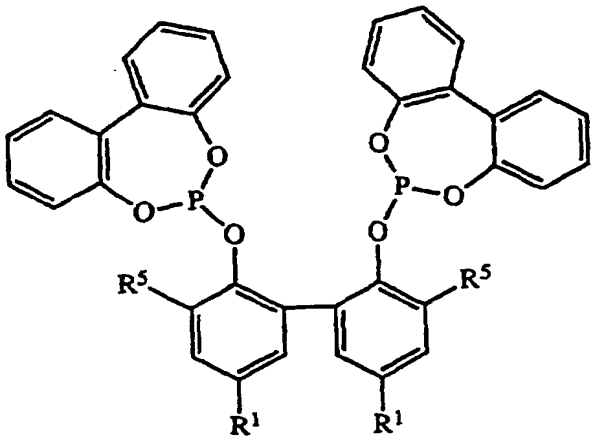
10. The process of Claim 9 wherein the Lewis acid promoter is $ZnCl_2$, $CdCl_2$, $B(C_6H_5)_3$, or $(C_6H_5)_3SnX$ wherein X is CF_3SO_3, $CH_3C_6H_5SO_3$ or $(C_6H_5)_3BCN$.

11. The process of Claims 1 or 2 wherein the reaction is carried out at a temperature of from 0 to 150°C and at atmospheric pressure.

12. The process of Claims 1 or 2 wherein each R^1 is OR^4 wherein each R^4 is methyl, and the monoolefin is 3-pentenenitrile.

13. The process of Claims 1 or 2 wherein each R^1 is OR^4, wherein each R^4 is methyl, and the monoolefin is 2-pentenenitrile.

14. A catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand of Formula I



I

wherein

each R^1 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl; and

each R^5 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms.

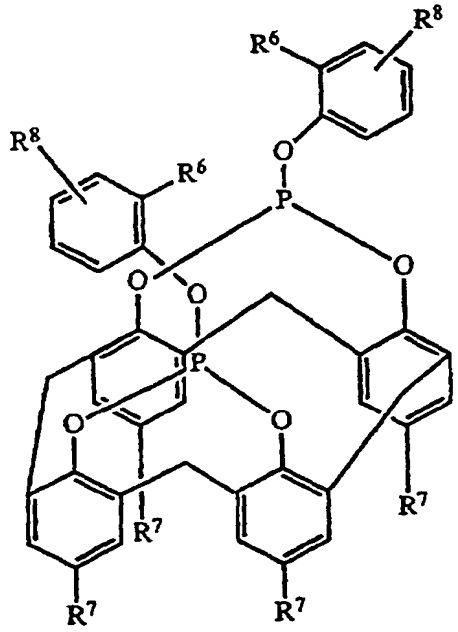
15. The catalyst precursor composition of Claim 14 further comprising a Lewis acid promoter.

16. The composition of Claims 14 or 15 wherein each R^1 is OR^4 wherein each R^4 is alkyl.

17. The composition of Claim 16 wherein each R^1 is OR^4 wherein each R^4 is methyl.

18. The composition of Claims 14 or 15 wherein each R^5 is a tertiary hydrocarbon containing 4 carbon atoms.

19. A catalyst precursor composition comprising zero-valent nickel and a bidentate phosphite ligand selected from the group consisting of Formula II, Formula III, Formula IV, and Formula V,

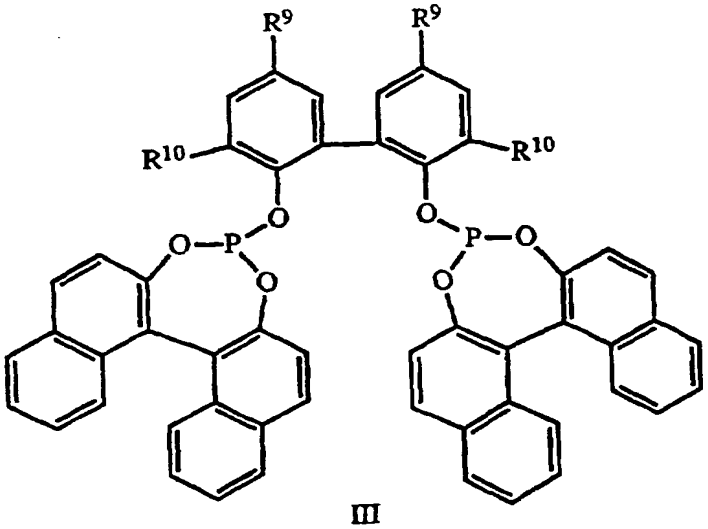


II

wherein

each R^6 and R^7 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms; and

each R^8 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl;

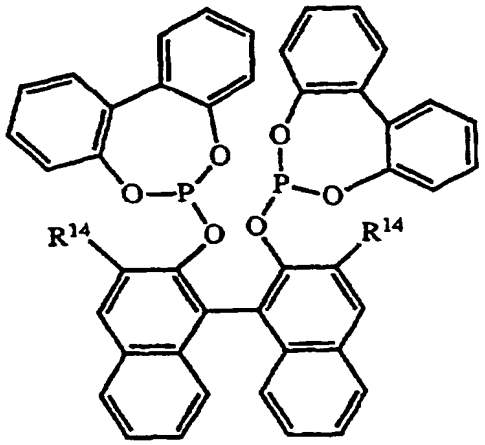


III

wherein

each R^9 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl; and

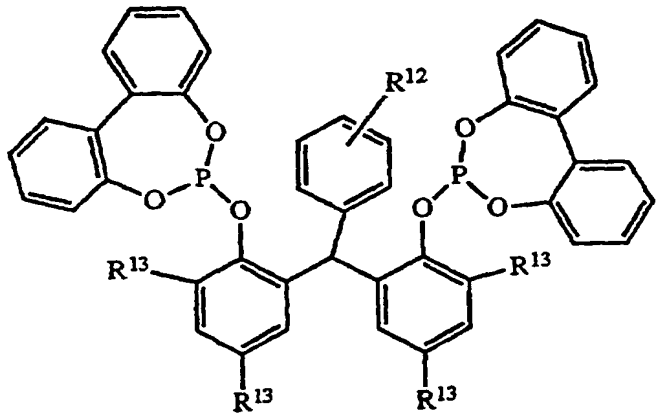
each R^{10} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms;



IV

wherein

each R^{14} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms or $Si(R^{11})_3$ where R^{11} is independently a branched or straight chain alkyl of up to 12 carbon atoms or phenyl; and



V

wherein

R^{12} is H or a branched or straight chain alkyl of up to 12 carbon atoms; and

each R^{13} is independently a branched or straight chain alkyl of up to 12 carbon atoms.

20. The catalyst precursor composition of Claim 19 further comprising a Lewis acid promoter.

21. The catalyst precursor composition of Claims 19 or 20 wherein Formula II is selected as the bidentate phosphite ligand and each R^6 and R^7 is t-butyl and R^8 is OCH_3 or H.

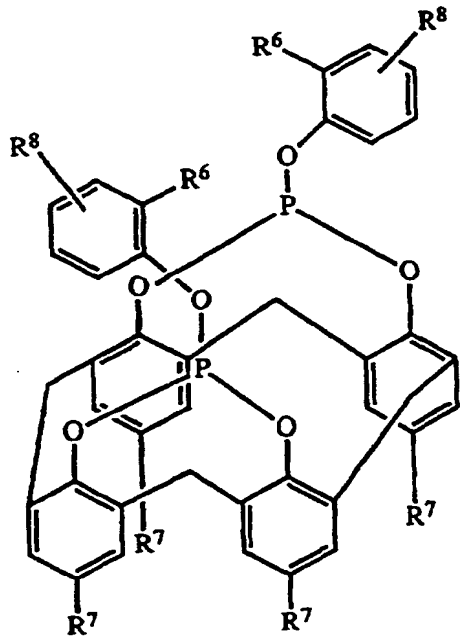
22. The catalyst precursor composition of Claims 19 or 20 wherein Formula III is selected as the bidentate phosphite ligand and each R^9 is OCH_3 and each R^{10} is t-butyl.

23. The catalyst precursor composition of Claims 19 or 20 wherein Formula IV is selected as the

dibentate phosphite ligand and each R^{14} is triphenyl silyl.

24. The catalyst precursor composition of Claims 19 or 20 wherein Formula V is selected as the bidentate phopshite ligand and R^{12} is H and each R^{13} is CH_3.

25. A process for hydrocyanation comprising reacting a nonconjugated acyclic aliphatic monoolefin, monoolefin conjugated to an ester group or monoolefin conjugated to a nitrile group with a source of HCN in the presence of a catalyst precursor composition comprising zero-valent nickel and bidentate phosphite ligand selected from the group consisting of Formula II, Formula III, Formula IV, and Formula V,

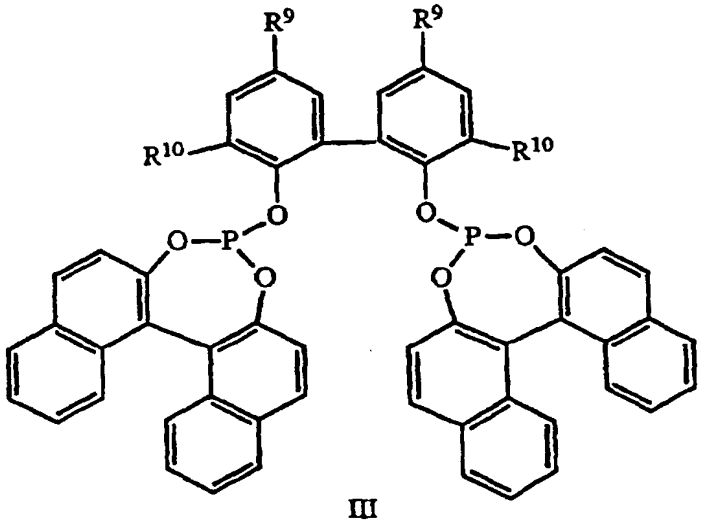


II

wherein

each R^6 and R^7 is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms; and

each R^8 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl;

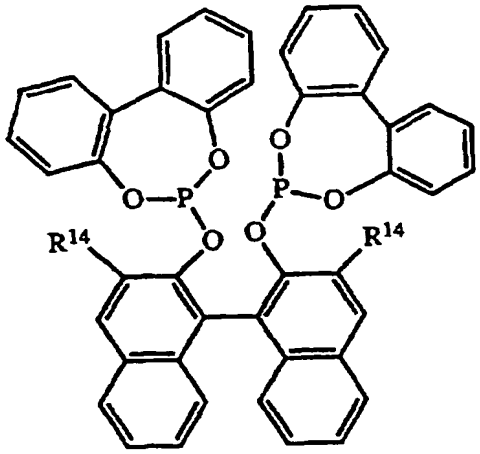


III

wherein

each R^9 is independently H or a branched or straight chain alkyl of up to 12 carbon atoms, or OR^4 wherein R^4 is C_1 to C_{12} alkyl; and

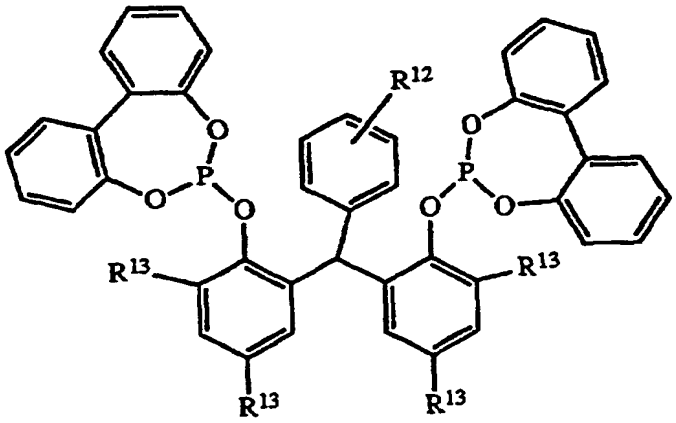
each R^{10} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms;



IV

wherein

each R^{14} is independently a tertiary substituted hydrocarbon of up to 12 carbon atoms or $Si(R^{11})_3$ where R^{11} is independently a branched or straight chain alkyl of up to 12 carbon atoms or phenyl; and



V

wherein

R^{12} is H or a branched or straight chain alkyl of up to 12 carbon atoms; and

each R^{13} is independently a branched or straight chain alkyl of up to 12 carbon atoms;

and wherein said reaction is carried out to produce a terminal organonitrile.

26. The process of Claim 25 wherein the reaction is carried out in the presence of a Lewis acid promoter.

27. The process of Claims 25 or 26 wherein Formula II is selected as the bidentate phosphite ligand and each R^6 and R^7 is t-butyl and R^8 is OCH_3 or H.

28. The process of Claims 25 or 26 wherein Formula III is selected as the bidentate phosphite ligand and each R^9 is OCH_3 and each R^{10} is t-butyl.

29. The process of Claims 25 or 26 wherein Formula IV is selected as the bidentate phosphite ligand and each R^{14} is triphenyl silyl.

30. The process of Claims 25 or 26 wherein Formula V is selected as the bidentate phosphite ligand and R^{12} is H and each R^{13} is CH_3.

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 94/12794

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C253/10 B01J31/18 C07C255/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, 1991, LETCHWORTH GB pages 803 - 804 M. J. BAKER ET AL. 'Chelating Diphosphite Complexes of Nickel(0) and Platinum(0): Their Remarkable Stability and Hydrocyanation Activity' cited in the application see the whole document ---	1,14,19, 25
A	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, 1991, LETCHWORTH GB pages 1292 - 1293 M. J. BAKER,P. G. PRINGLE 'Chiral Aryl Diphosphites: a New Class of Ligands for Hydrocyanation Catalysis' cited in the application see the whole document ---	19,20,25

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 February 1995	- 6. 03. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Seufert, G

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 94/12794

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,93 03839 (UNION CARBIDE CHEMICALS & PLASTIC TECHNOLOGY CORP.) 4 March 1993 cited in the application see page 6, last paragraph - page 7, line 13; examples 1-8,42-44	1,14,19, 25
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol.115, 1993, WASHINGTON, DC US G. D. CUNY, S. L. BUCHWALD 'Practical, High-Yield, Regioselective, Rhodium-Catalyzed Hydroformulation of Functionalized .alpha.-Olefins' cited in the application see page 2067, compound 1	14,19

1

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INTERNATIONAL SEARCH REPORT

Intern: al Application No
PCT/US 94/12794

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9303839	04-03-93	US-A-	5360938	01-11-94
		AU-A-	2507792	16-03-93
		EP-A-	0600020	08-06-94
		PT-A-	100797	29-10-93

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